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CONTRACT INSPECTION REPORT

25X

TO:

ENGINEERING SECTION/CB/PD/OL

DATE

8 Sept. 1964

INSPECTION REPORT NO. (If final, so state)

1

ESTIMATED COMPLETION DATE

August 1965

NAME OF CONTRACTOR

TYPE OF COMMODITY OR SERVICE

Non-Reversible Color Recording

THE CONTRACTOR IS ON SCHEDULE



YES



NO

PER CENT OF WORK COMPLETED

2%

THE CONTRACTOR WILL PROBABLY REMAIN WITHIN ALLOCATED FUNDS ☒ YES ☐ NO IF ANSWER IS "NO" ADVISE RECOMMENDATION AND/OR ACTION OF SPONSORING OFFICE, ON REVERSE HEREOF. IF KNOWN, INDICATE MAGNITUDE OF ADDITIONAL FUNDS INVOLVED.

HAS AN INTERIM REPORT, FINAL REPORT, PROTOTYPE, OR OTHER END ITEM BEEN RECEIVED FROM THE CONTRACTOR DURING THE PERIOD? ☐ YES ☒ NO (If yes, give details on reverse side.)

HAS GOVERNMENT-OWNED PROPERTY BEEN DELIVERED TO CONTRACTOR DURING THIS PERIOD? ☐ YES ☒ NO (If yes, indicate items, quantity, and cost on reverse side.)

OVERALL PERFORMANCE OF CONTRACTOR

1. ☐ OUTSTANDING3. ☒ ABOVE AVERAGE5. ☐ BELOW AVERAGE 7. ☐ UNSATISFACTORY2. ☐ EXCELLENT4. ☐ AVERAGE6. ☐ BARELY ADEQUATE

IF OVERALL PERFORMANCE OF CONTRACTOR IS UNSATISFACTORY OR BARELY ADEQUATE, INDICATE REASONS ON REVERSE SIDE.

RECOMMENDED ACTION



CONTINUE AS PROGRAMMED



WITHHOLD PAYMENT PENDING SATISFACTORY PERFORMANCE



TERMINATE



OTHER (Specify)

IF TERMINATION IS RECOMMENDED OR IF THIS IS A FINAL REPORT ATTACH COMMENTS IN NARRATIVE FORM ON CONTRACTOR'S PERFORMANCE AND CERTIFY THAT ALL DELIVERABLE ITEMS UNDER THE CONTRACT HAVE BEEN RECEIVED. THESE INCLUDE, WHERE APPLICABLE, THE FOLLOWING:

ITEM	REC'D	DOES NOT APPLY	ITEM	REC'D	DOES NOT APPLY
PROTOTYPES			MANUALS		
DRAWINGS AND SPECIFICATIONS			FINAL REPORT		
PRODUCTION AND/OR OTHER END ITEMS			SPECIAL TOOLING		
			OTHER GOVERNMENT PROPERTY		

DATE OF LAST CONTACT WITH CONTRACTOR

13 Aug. 1964 (visit)

SIGNATURE OF INSPECTOR

DIVISION

25X1

Final Report

Black and White Films

30 August 1965



25X1

ABSTRACT

The progress made in the first year's effort in the development program for a black and white, dry processed, photobleached film is summarized. Experimental techniques have been developed for the preparation, exposure, and evaluation of films. Evaluation of film speeds in terms of the quantum efficiency is found to be the most useful method available, as it is more generally applicable than the kinetic evaluations used previously.

One hundred sixty-eight dyes have been tested, with dyes in the anthraquinone and methine classes showing the most useful properties. Several photosensitive agents have been tried, of which iodoform and carbon tetrabromide are most useful. The dependence of quantum efficiency and of rate of reaction on the concentration of dye, on the concentration of photosensitive agent, on wavelength, on intensity, and on time have been measured. Studies have been undertaken to determine the mechanism of the reaction. The most probable mechanism for the anthraquinone dyes involves the formation of a strong acid which reacts with the dye.

A general discussion of methods of presenting film speeds for photobleaching materials is given. It is shown that similar comparisons can yield widely differing numbers, depending on the conditions chosen. By a conservative method, film speeds of 2.5×10^{-7} to 3×10^{-6} are found for single dyes. A black and white film has been developed and evaluated, and has a speed of 1.4×10^{-8} . Future work will be directed primarily at the achievement of a multiplicative factor to allow greater film speeds.

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I. INTRODUCTION

This report summarizes the results of the first year's effort on the Black and White Film project. The objective of the work is to assess the potential of the previously demonstrated dye bleaching process so as to produce a film having the desired color, optical density range and sensitivity. The objectives to be attained ultimately by the process can be summarized as follows:

- A. Black and white (or colorless) film, with $D_{\max} = 3.0$ or more over the visible region, and $D_{\min} = 0.05$ or less.
- B. Resolution capability of 400 line pairs/mm.
- C. ASA speed equivalent to 0.1.
- D. Ability to control the photographic characteristic curve so as to vary gamma from 0.8 to 2.5
- E. Material must be stable in storage, both before and after exposure, for periods greater than a year, at ordinary temperatures and humidity.

The strategy of the first year's program consists, first, of screening large numbers of dyes for their bleaching properties, second, determination of the molecular structural factors associated with good bleaching behavior, third, determination of the mechanism(s) of the bleaching reaction, and last, the use of the information thus obtained in designing systems with superior properties. This report will summarize the progress made toward achieving the first year objectives, and the extent of the information obtained by the strategies listed above. The experimental techniques used throughout the program will be described first, followed by a description of the techniques used for analysis of the data, and a discussion of the assumptions and conventions used in setting up the formulas. In succeeding sections, the various subprograms will be described: the materials survey, the study of reaction mechanisms, the relationship between rates of reaction and variables such as concentration and age of samples (herein called parametric studies), and the practical photographic properties of the films which have been prepared. In the last section, the significance of the results described to the direction of the continuing program of development of these materials will be discussed.

II. EXPERIMENTAL TECHNIQUES

The materials of interest are usually examined as solutions or suspensions in a polymer film on a glass slide. The slides are exposed to light, and the resulting changes in optical density measured and evaluated. The techniques involved in slide preparation, in exposure, and in data readout will be described.

A. Slide preparation. The materials involved in a preparation are a dye, a photosensitive agent, and a polymer binder. The specific materials used will be discussed in the section "Materials Survey" below. The standard technique for casting films is as follows. A solution is made up of the polymer in an appropriate solvent. To this is added weighed amounts of dye and photosensitive agent. A few drops are placed on a slide and distributed evenly over the surface. The excess is then drained off. The slide is dried in an oven at 75°C under a glass frit to which a few drops of solvent have been added. This technique yields relatively smooth, clean films, when the concentrations have been correctly chosen. The thickness of the slide is determined by the proportions of polymer to solvent, while the dye concentration is determined by the ratio of dye to polymer. Dye concentration is calculated from the measured absorbance of the film.

B. Exposure. Three techniques are used for exposing the slides to light. In the initial screening procedure, the slide is put into a slide projector, in the usual projection position, and exposed for an arbitrary time. It is then visually examined. For samples with large apparent color changes, an absorption spectrum is obtained, using a Beckmann spectrophotometer, before and after exposure.

For more quantitative work, the apparatus described in Progress Report #3, September 1964, is used. In brief, the apparatus functions by moving a slide into and through a beam of light, which may be monochromatic, or may be white light. Both before and after exposure, the absorption of monochromatic light at the wavelength of maximum absorption of the dye is measured as a function of distance along the slide. This is done by moving the slide past a narrow slit while monitoring the intensity of transmitted monochromatic light by means of a photomultiplier.

This technique of obtaining the rate of dye bleaching has several advantages. It is simple, rapid, and results in a sample in which the effect of variation in exposure may be visually examined as well as measured instrumentally. The method is useful, however, only for experiments in which high accuracy is not important, because it is difficult to incorporate corrections due to variations in slide thickness in the calculations.

When it is necessary to achieve high accuracy, a stationary sample is used, and a small area of the sample is illuminated by the desired light, which may be white or monochromatic. The transmitted light is monitored by a photomultiplier, as above, with a recording potentiometer. If white light is used, a monochromator is placed between the sample and the photomultiplier so that only light of the chosen wavelength is monitored.

The records produced by either of the above techniques consist of a strip chart; giving the intensity of the transmitted light, I , as a function of time. The rate of travel of the strip chart of the recorder has been calibrated, so that the duration of exposure at any point is known. The photomultiplier is adjusted so that full scale corresponds to 100% transmittance. The absorbance, A , defined as $\log I_0/I$, i. e. $\log 100/I$, where I_0 is intensity of incident light, is proportional to the concentration of the absorbing species.

25X1 The light sources used are a 300W slide projector, for initial screening, and a 500W projector for the quantitative work. The 500W projector and the monochromator, high intensity grating monochromator, are mounted on metal plates so that the orientation of the equipment can be exactly reproduced. For the stationary sample technique, a slit machined into the exit slit housing of the monochromator serves to hold the slide during exposure. The photomultiplier is a Gamma Scientific Log-Linear photomultiplier photometer, with three linear decade ranges of sensitivity, and a five decade logarithmic range. The energy output of the 500W lamp has been calibrated by means of a twelve junction Eppley thermopile. The output of the lamp-monochromator combination has been similarly calibrated as a function of wavelength.

The response of the lamp-monochromator combination is similar to that of the eye, in that it is peaked at 5500 Å, but the peak is not as sharp.

C. Heat fixing. After exposure, the samples may be subjected to heat fixing if they are to be preserved, or projected. Heat fixing is accomplished by placing the samples in an oven at a temperature and time determined by the volatility of the photosensitive agent. Since the binding ability of the various dyes and polymers is quite variable, volatility may vary from one mixture to another. The time and temperature for a given mixture is determined by heating a series of samples of the mixture, each under different conditions, and determining the mildest conditions after which the sample will not bleach during a prolonged exposure.

A second method of heat fixing consists of exposing the sample to an infrared lamp, while protected from visible radiation with an appropriate filter, such as a Wratten 89B. A typical set of heat fixing conditions is that applicable to the black film discussed later in this report, namely, oven heating at 160° for ten minutes or at 110° for two hours, or exposure to the 200W heat lamp at two inches for seven minutes. These conditions pertain to a film based on CBr_4 . The conditions for a CHI_3 based film are milder. To reduce the times and temperatures even further, more volatile agents must be used, or the use of vacuum in heat fixing investigated. Other heating techniques, such as dielectric heating, may prove superior, and should be explored as future work.

III. ANALYSIS OF DATA

During the major portion of the contract year, the standard procedures of chemical kinetics were used to manipulate the data and to derive rate constants with which to characterize the various formulations. These procedures, described in detail in Progress Report #8, February 1965, page 2, consisted of applying standard zero-order kinetic analysis to films of high optical density and first-order kinetics to films of low optical density. These techniques gave results which were useful in characterizing the individual formulation, and which gave correlations between different formulations, but the precision of the results and of the correlations was not entirely satisfactory.

In July, in an effort to reconcile the data at which and low optical densities, and to handle data at intermediate densities, a new approach was taken. The basic assumption was made that the quantum efficiency (the fraction of photons absorbed by dye molecules that caused reaction to take place) was constant throughout a particular run. Many of the key runs have been recalculated on this basis. There has not yet been sufficient time to evaluate this approach thoroughly, however.

If the quantum efficiency ϕ is constant, then $-dc/dt = \phi I_{\text{abs}}$, where I_{abs} is the intensity of the light absorbed by reacting molecules, in units of einsteins (moles of photons) per cm^2 per sec., and dc/dt is the change in concentration of dye molecules with time, in moles per cm^2 per sec. Integrating this equation, we get $\Delta c = \phi I_{\text{abs}} \Delta t$, that is, the change in concentration of dye, Δc , during a short time interval, Δt , is proportional to the average absorption during that time interval. This simple result is obtained by making the time interval short enough so that one can approximate I_{abs} over the time interval by the average value \bar{I}_{abs} during the interval.

The units used for concentration above are moles per cm^2 . By this is meant the number of moles in that volume of film that consists of one cm^2 of surface area of the film, multiplied by the thickness of the film, which is usually not measured. This choice of units arises from the following considerations. Beer's law relates the absorbance, A , to the concentration, c , by

$$A = \log I_0 / I = \epsilon c d$$
, where ϵ is the absorptivity or the extinction coefficient and d is the thickness of the material in the direction of the light path. From this relation, we see that A specifies only the product $c \cdot d$, which is determined by the number of particles per unit cross-sectional area normal to the light beam. For this reason, and also because our light sources are calibrated in terms of energy falling on unit area of surface, it is convenient to use the units of moles / cm^2 for c . Similarly, ϵ is in units of cm^2/mole , since A is a dimensionless quantity. Thus, the values of ϵ quoted herein are a factor of 1000 larger than the molar extinction coefficients usually quoted in the literature, because of the difference in concentration units used.

Plotting $\Delta c / \Delta t$ against \bar{I}_{abs} should give a straight line with slope equal to the quantum efficiency. Several of the runs plotted give straight lines, as in the example of this type of plot given in Figure 1. In most of the runs, however, the extrapolation of the curve does not go through the origin, as one might expect. The reason for this is not yet clear. It may lie in the technique used for evaluation Δc , which involves several assumptions. These are, first, that the light absorbed at the wavelength used (the wavelength of maximum absorption of the original dye) is absorbed only by the dye and the photoproduct. Second, the ratio of extinction coefficients of these two materials is given by the ratio of the initial and final absorbances. Third, the fraction of light absorbed by each species is similar to what it would be in a stirred solution at the same concentrations.

It should be noted that in the limit of high optical density, say $D > 1.5$, the zero order kinetics should give the same results as the quantum efficiency calculations, since I_{abs} is constant. Similarly, at the limit of very low optical density, say $D \leq .04$, first order kinetics should give similar results, since in this limit I_{abs} is directly proportional to c :

$$a c d = \log I_o / I = \log(1 - \frac{I_o - I}{I}) \approx \frac{I_o - I}{I} = \frac{I_{\text{abs}}}{I} \text{ for } \left[\frac{I_o - I}{I} \right] \ll 1$$

However, most of the experimental results are in regions of concentrations where these approximations are quite poor.

A discussion of the calculation of film speed, or sensitivity, is incorporated in the section on photographic properties of the films.

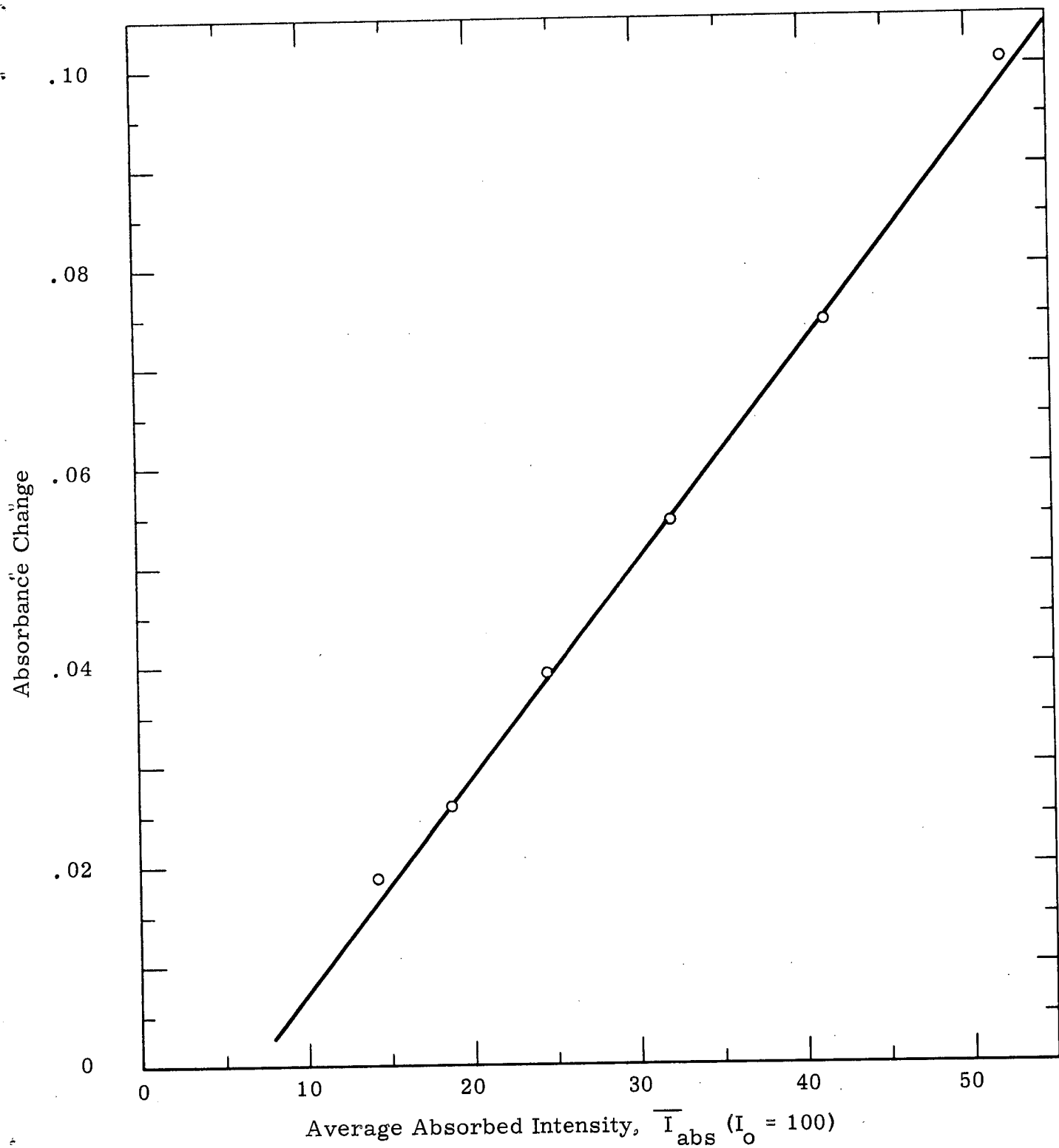


Figure 1. Quantum Efficiency Plot

IV. MATERIALS SURVEY

To date, 168 dyes have been tested in some 415 formulations. These are primarily samples of commercial dyes obtained from manufacturers, such as Allied Chemical, duPont, General Aniline and Film, and several others. The commercial samples contain fillers and other impurities, and therefore cannot be used for precise quantitative measurements. Several of the other dyes have been purchased. In addition, a group of pure dyes of the anthraquinone class have recently been obtained as samples from duPont. These have not yet been studied.

The dyes used are representative of the following classes:

anthraquinone	41
arylmethane	17
azo	42
methine	25
oxazine	5
xanthene	14
miscellaneous	24

Of these, the methine and the anthraquinone dyes have been the most successful and the most thoroughly studied.

The photosensitive agents used have been iodoform (CHI_3), carbon tetrabromide (CBr_4) and trichloromethylsulfonylchloride (TCSC). TCSC proved to be not as widely applicable as CHI_3 and to give less reproducible results. Work was restricted to CHI_3 for the major portion of the program.

CHI_3 has the disadvantage of producing a dark yellow or tan product on exposure to light. CBr_4 , although it seems to be somewhat less sensitive than CHI_3 , gives less of a background color, and was used extensively in the last months of the program. It is less volatile than CHI_3 , however, and the heat fixing properties are correspondingly poorer. A few other materials were also tried briefly, but did not prove as useful as the above compounds.

The dye and photosensitive agent are cast into a film in a polymer matrix. The polymers used have been polystyrene, saran (polyvinylidene chloride), Carboset (an acrylic resin), polyvinyl chloride (PVC), and polyvinylpyrrolidone (PVP). The polymers have been chosen primarily for convenience as good solvents for the dyes and for ease in casting slides. Requirements which must be met in the ultimate polymer matrix are that it be dimensionally stable during the heat fixing process, and that it not melt, causing loss of resolution. These requirements can be met in a variety of ways, as by use of high molecular weight polymers, or of thermosetting polymers. No serious effort has been applied to the problem as yet.

It is interesting to note that, whereas in most cases light must be absorbed by the photosensitive agent to be effective in bleaching the dye, in the case of the anthraquinone and methine dyes absorption by the dyes themselves can lead to bleaching, in mixtures with the photosensitive agents. In films of dye alone, the same absorption does not lead to any photoreaction. The same phenomenon is observed in a few isolated instances of other dyes.

V. PARAMETRIC STUDIES

Many studies were made of the effect of dye and of CHI_3 concentration, wavelength, aging, and similar factors on rates of photobleaching. The data was analyzed in terms of rate constants, which are significant only in comparing films with similar concentrations. Some of the runs, as mentioned above, have been recalculated in terms of quantum efficiencies. The most significant conclusions from both types of calculation will be summarized in this section.

A. An extensive series of tests with one formulation of an anthraquinone dye with CHI_3 , keeping CHI_3 concentration constant, showed that the quantum efficiency of the photobleaching reaction was independent of dye concentration over a range of 30 to 1, when light is absorbed by the dye only.

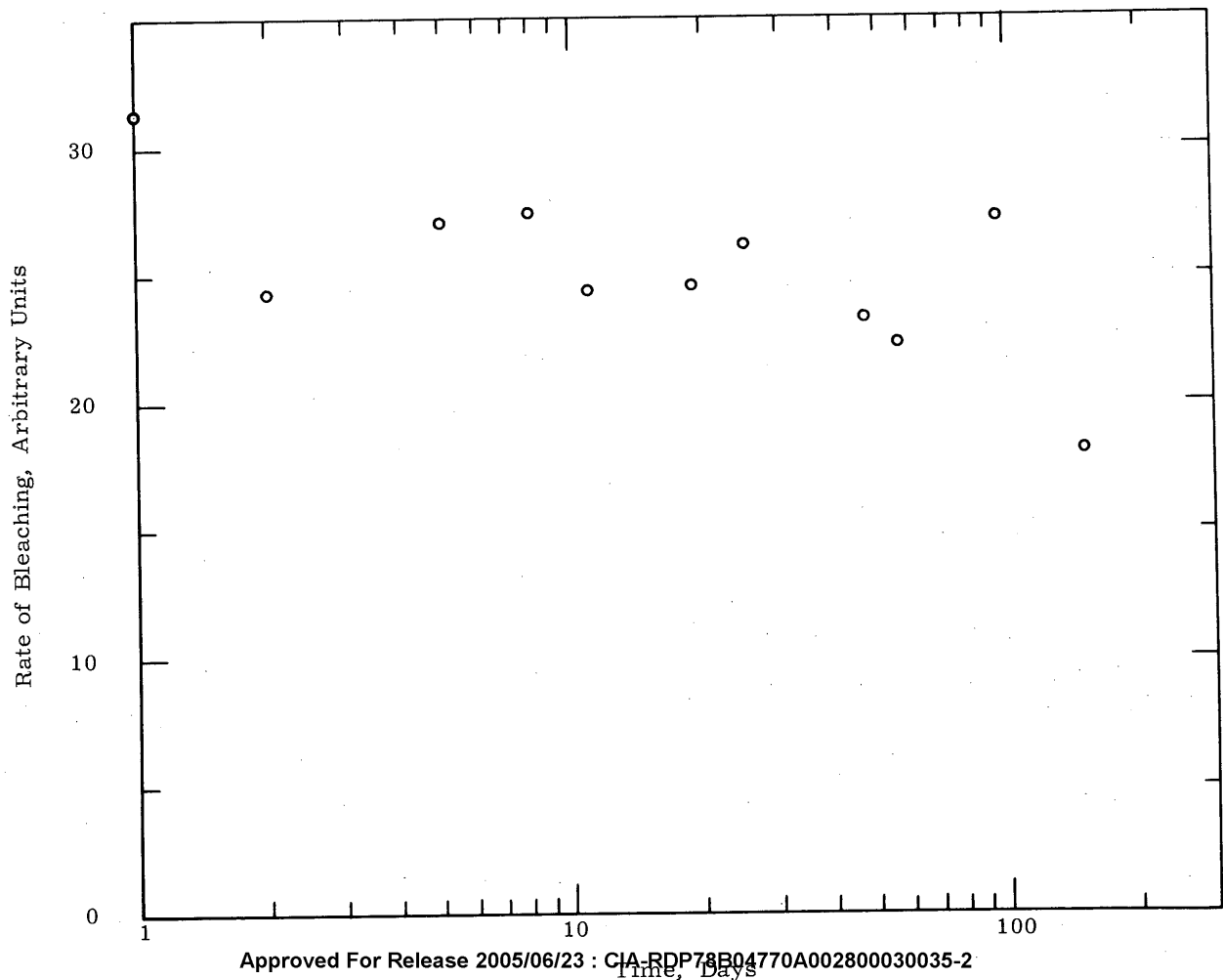
B. A series of runs in which dye concentration was kept constant while CHI_3 concentration was varied by 20 to 1 showed quantum efficiency proportional to CHI_3 concentration. Absorption was at the dye wavelength.

C. A series of dyes, each made up with CHI_3 , showed greater rates of bleaching when illuminated at 3600 \AA , the iodoform absorption peak, than when illuminated at the dye wavelength. The ratio of quantum efficiencies seems to be of the order of 10. The exact quantum efficiencies have not been calculated.

D. A series of runs on a single formulation, with absorption at the dye, wavelength, but with intensity of illumination varying over a range of about ten to one, indicates that the rate is independent of intensity.

E. The effect of aging of films was investigated. The results are shown in Figure 2. As can be seen in that figure, a fairly steep initial decrease in sensitivity is followed by a slower decrease.

F. The action spectrum of a dye which bleaches through its own absorption was measured. The extent of reaction closely paralleled the absorption spectrum of the dye, implying that quantum efficiency is relatively constant across the absorption band of the dye.



VI. MECHANISM STUDIES

The mechanism of the photobleaching reaction has been studied with a view toward designing a system which could supply a multiplicative factor to the photographic speed, similar to the function of development in conventional silver halide photography. That a multiplicative factor of 10^2 to 10^7 is needed is shown by the calculation made in the next section that a system with quantum efficiency of one and extinction coefficients around 2×10^8 mole/cm² will give an ASA equivalent or $S_p^{0.1}$ of about 1.4×10^{-3} , and the film discussed later in this report has an $S_p^{0.1}$ of 1.34×10^{-8} . To get the desired speed of 0.1, a speed multiplying factor must be introduced.

The present hypothesis as to the mechanism of the reaction, in the methines and anthraquinones at least, is that the dyes behave as strong bases when illuminated. For example, they are presumed to react with iodoform as a very weak acid, causing it to decompose with formation of the strong acid HI. This in turn bleaches the dye by reacting with it to form a salt. In the case of CBr₄, which when photoactivated can react with proton donors to form HBr, the activation energy can be transferred from the excited state of the dye, caused by photon absorption. In this case the HBr bleaches the dye.

Substantiation of the proposed mechanism may be found in the calculated results that excited singlet states of aromatic amines are very strong bases.¹ Differences from the ground state of up to 6 pK units have been observed. The quinone groups on the adjacent rings in the anthraquinones would be expected to enhance the effect further. There does not seem to be any evidence in the literature on the excited state basicity of the complex heterocyclic rings found in the cyanine dyes.

The experimental evidence for this mechanism is not conclusive. Further work planned for the immediate future should provide a definitive answer. The evidence for the mechanism obtained thus far is as follows.

A. The quantum efficiency of the methine dyes and of the anthraquinones increases with increasing basicity of the dyes. This may indicate that the ease of reaction with acid is a determining factor, although, as pointed out in Progress Report #8, February 1965, it may also indicate that a reduction is taking place.

B. The change in spectrum of some dyes on addition of acid shows marked similarity to the change on photobleaching.

C. In some cases, addition of base can cause a partial reversal of the photobleaching reaction.

The mechanism studies to be performed will investigate the generality and the extent to which the last two statements above apply.

1. G. Jackson and G. Porter, Proc. Roy. Soc. London A260 13 (1961)

The significance of the mechanism to the search for a multiplicative factor for amplifying the effect of a photon is simply that it points out the direction of the research most likely to succeed. To illustrate, let us consider some of the alternative reaction mechanisms and their implications. Let us assume that the reaction is one in which an acid reacts with the dye, as above. The primary step in the reaction is the absorption of a photon by the dye or by the photosensitive agent (PSA). In the case of absorption by the dye, there are several possibilities for the second step. First, mechanism I, the excited state of the dye can react with the PSA, or some complex of PSA and solvent, abstracting a proton and causing decomposition of the PSA. Second, mechanism II, the dye can transfer energy in a photosensitization process to the PSA, which then decomposes by (A) a free radical process or (B) an ionic process to yield acid plus other reaction products. In the case of light absorbed directly by the PSA, mechanism III, energy is obtained directly from the photon for decomposition by (A) a free radical process or (B) an ionic process, or, mechanism IV, energy is transferred to the dye which then can react as in mechanism I. If, however, an acid-base reaction as such is not involved, a whole new set of mechanisms may obtain.

The implications of the several possible mechanisms for an acid-base reaction lie in means to increase the primary quantum efficiency, by decreasing any barriers to reaction which may exist. Similar statements may be made if the major mechanism is free radical formation, or oxidation or reduction. It may, however, turn out that a knowledge of the major mechanism is sufficient for an attack on the problem of finding an amplification process, and that knowledge of the detailed mechanism, as in those enumerated above, is not essential for this purpose. Thus, for acid-base reactions, the problem of finding an amplification factor is that of finding some method of producing a large number of protons with a single photon. This can be done, for example, in radiolysis of polyvinyl chloride, where quantum efficiencies around 25 have been observed. However, the observed efficiency in photolysis is much less, due to low efficiency of the primary step. If one can make the primary step more efficient, as by modifying the chemical structure, one can then increase the speed of the over-all process. However, it would be inefficient to undertake this investigation before it is definitely shown that acid-base reactions are involved in the process. Similarly, chain reactions of free radicals are known, where a single initiating event leads to a large number of reaction events. The successful propagation of such a chain in the rigid matrix of a film promises to be difficult, and should not be attempted until it is clear that it would be appropriate to the photobleach process.

VII. PHOTOGRAPHIC PROPERTIES

A. General. The photographic properties of most concern to date have been speed or sensitivity. One problem that has led to considerable discussion, without a really satisfactory conclusion, is that of how to express photographic sensitivity of materials which bleach. In the usual method for silver halide films, speed is taken as the reciprocal of the exposure in meter-candle-seconds (mcs) necessary to produce a density of 0.1 above fog. In our samples, which have optical densities varying more or less widely across the visible region of the spectrum, depending on the individual dye or mixture of dyes used, the process is one of bleaching rather than darkening. Further, the form of the relationship between optical density and exposure for these materials and for silver halide materials is different. Consequently, results of a comparison of photobleaching films and silver halide films will depend on the conditions chosen for the comparison.

An example of this is given by using two sets of conditions in the same comparison formula. The formula proposed on page 5, Photobleach Photography, Phase II Proposal is

$$S_p^{3.0} = N_s^{3.0} / N_p^{3.0}$$

where $S_p^{3.0}$ is the calculated sensitivity of the photobleach materials, $N_p^{3.0}$ is the number of incident photons calculated to be necessary to bleach a sample from an optical density of 3.0 to 0, and $N_s^{3.0}$ is the number of incident photons at 5500 A necessary to produce an optical density of 3.0 above fog in a silver halide film of ASA = 1, gamma = 1, calculated on the basis of 680 lumens per watt at 5500 A. If the optical density is 0.1, i. e., the film is bleached from density 3.0 to 2.9, or from 1.0 to 0.9, etc., and the silver halide film goes to 0.1 above fog, the formula would be

$$S_p^{0.1} = N_s^{0.1} / N_p^{0.1}$$

i. e., the suffixes refer to the optical density change used for the calculation. The number of photons is used, rather than energy, so that monochromatic exposures made at different wavelength can be compared. The photon ratio for exposures at two wavelengths is equal to the energy ratio times the reciprocal of the wavelength ratio.

The formula based on $D = 3$ probably corresponds most closely to the ultimate conditions of use, since eventually photobleach films will have an initial density of about three. However, there are inaccuracies involved in

the extrapolation from films of lower density. For example, it has not yet been shown that quantum efficiency remains constant at densities greater than one.

Let us calculate the sensitivity, $S_p^{3.0}$ and $S_p^{0.1}$, for a film of maximum sensitivity but without any multiplicative factor. For the reference silver halide film, N_s is given by the number of photons in an exposure of 1 mcs at 5500 A,

$$1 \text{ mcs} = 10^{-4} \text{ lumen-sec/cm}^2 = 1/680 \times 10^{-4} \text{ w-sec/cm}^2 \\ = 1.47 \text{ erg/cm}^2$$

$$1 \text{ einstein} = 6.02 \times 10^{23} \text{ photons has an energy of} \\ 2.17 \times 10^{12} \text{ erg at 5500 A}$$

Therefore,

$$1 \text{ mcs} = \frac{1.47}{2.17 \times 10^{12}} \times 6.02 \times 10^{23} = 4.08 \times 10^{11} \text{ photons}$$

If $\gamma = 1$, $dD/d \log E = 1$, and therefore $E = 800 \text{ mcs}$ for $D = 3$. The number of photons is then $N_s^{3.0} = 3.27 \times 10^{14}$.

For the photobleach film, assume an extinction coefficient a of $2 \times 10^8 \text{ cm}^2/\text{mole}$, which is near the upper limit that we have measured. Let us also assume quantum efficiency of one. From Beer's law, $D = ac$, as in Section III above, and $\Delta D = a \cdot \Delta c$. But $\Delta c = \phi N_p^{0.1} / 6.02 \times 10^{23}$. That is, the change in concentration of dye molecules in the film (in moles/cm²) equals the number of effective photons/cm² divided by the conversion factor from moles to photons. Therefore,

$$N_p^{0.1} = \frac{6.02 \times 10^{23} (\Delta D)}{a \phi} = \frac{6.02 \times 10^{23} \times 0.1}{2 \times 10^8 \times 1} = 3 \times 10^{14}$$

Similarly, $N_p^{3.0} = 9 \times 10^{15}$

$$\text{Therefore, } S_p^{0.1} = 4.08 \times 10^{11} / 3 \times 10^{14} = 1.36 \times 10^{-3}$$

$$S_p^{3.0} = 3.27 \times 10^{14} / 9 \times 10^{15} = 3.63 \times 10^{-2}$$

and

$$S_p^{3.0} / S_p^{0.1} = 26.6$$

It is apparent, then, that the number one derives for the sensitivity of a photobleach film depends on the method of calculation. It also depends on the film taken as reference. For example, if the reference film had been chosen with gamma of 2, the ratio $S_p^{3.0}/S_p^{0.1}$ would be equal to one.

While the numbers one derives using $S_p^{0.1}$ are much less impressive than those using $S_p^{3.0}$, we use $S_p^{0.1}$ in this report as being a more conservative figure, and also because the data are experimentally accessible and do not require extrapolation. If one wishes to convert to $S_p^{3.0}$ values, one multiplies the stated sensitivity by 26.6.

The above development is strictly valid only for films exposed to monochromatic light. This will be the case for evaluation of samples of a single dye. For mixtures exposed to white light, one should determine an action spectrum and integrate the results with respect to wavelength. This is a lengthy and complex process, and for routine evaluation, we have adopted a less cumbersome technique, similar to that for silver halide materials. Using white light, i. e. a tungsten source, and the photomultiplier having peak response at 5500 Å mentioned above, we take the sensitivity to be $S_p^{0.1} = 1.47 \times 10^{-7}/E$, with the exposure, E , in joules/cm², giving a density change of 0.1. This procedure reduces to that described above when all wavelengths are equally effective, and the average energy of the photons is known.

B. Single dyes. Early in the project, one of the anthraquinone CHI_3 films was exposed to a helium-neon laser beam. The rate of bleaching data indicated an ASA equivalent of about 0.5 to 0.06, as compared to silver halide films. Calculations from tungsten exposures, however, gave much lower figures. Two attempts were later made to repeat the laser experiment. Neither attempt was successful. We therefore use the tungsten data to determine dye sensitivity. The experiments summarized here were made using monochromatic light at the dye absorption wavelength. It should be noted that absorption at the photosensitive agent wavelength is an order of magnitude more effective.

A silver halide film, ASA 0.0016, was exposed to monochromatic light in the moving sample apparatus, developed, and read out. The results were compared to those for six dye-iodoform films, each exposed at a single wavelength. The $S_p^{0.1}$ values for the samples used ranged from 2.5×10^{-7} to 3×10^{-6} . The values obtained by direct comparison of exposures with the silver halide film agreed very well with those obtained by calculation of absolute exposure.

C. Black and white film data. The mixture chosen for the black and white film for evaluation consists of Indophenol Blue, Celliton Fast Pink FF3BA and PABR (i. e., 5-(p-dimethyl-aminobenzylidene)-rhodanine) and CBr_4 , with weight ratio of 4:3:2:120, in polyvinylchloride. The absorption spectrum of a typical film is shown in Figure 3, before and after exposure to white light. D_{max} for this film is 1.52, and D_{min} is 0.32, as determined by use of the photomultiplier system described above.

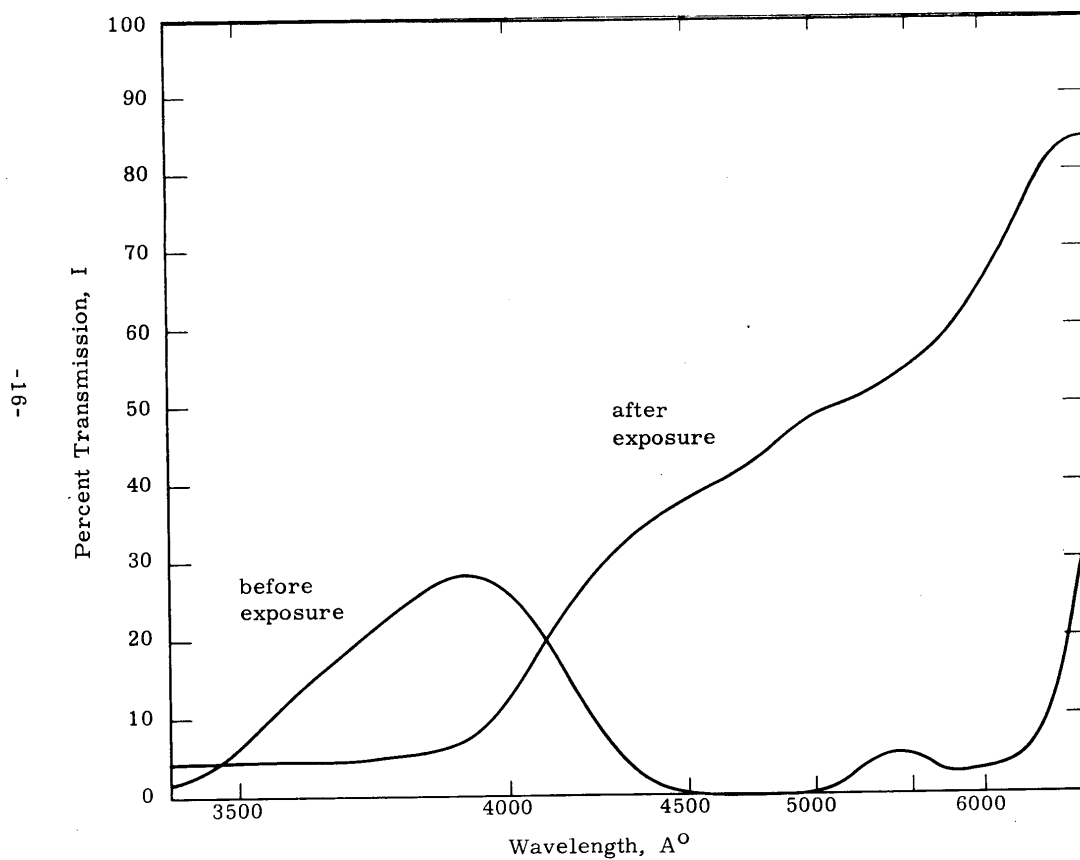


Figure 3. Absorption Spectrum of Black and White Film
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A typical H&D curve is shown in Figure 4. Overlapping curves are obtained for runs with intensity varying by a factor of four, i. e., from 0.06 w/cm^2 to 0.24 w/cm^2 . The $S_p^{0.1}$ for this film is seen from the figure to be $1.47 \times 10^{-7}/11 = 1.34 \cdot 10^{-8}$.

Reproduction of pictures printed with this film are shown in Figures 5a and 5b. Figure 5a shows the copy as taken, and Figure 5b after heat fixing. The speckled appearance of the sky areas in the film is due to uneven thickness of the film as cast, due to limited experience with the polymer used. A sample of a heat fixed picture is enclosed in the envelope mounted as Figure 6.

To summarize the results with this particular mixture, a film has been produced which is a step in the direction of the desired end product. The film has a good black color, can be made as dense as desired, but does not bleach as completely as is necessary. The photographic speed is too low, and while the resolution of the film is satisfactory, the heat fixing process probably degrades the resolution. The remedies for these defects will be sought in the second year's program, as described in the next section.

Three dyes were used to achieve a fairly uniform absorption throughout the visible spectrum. However, this also implies three photoproducts, which may account for some of the color remaining on the film after bleaching. The use of one or perhaps two dyes would be preferable. We have not, however, found a dye as yet which gives a satisfactory black film and which also bleaches; and manipulating the proportions of materials in a two-dye system to yield a good black seems to be much more difficult than in a three-dye system.

The interactions between the dyes have proven to be important. In the black film described above, we have shown that illumination in the absorption band of PABR will bleach the Indophenol Blue. Such symbiotic effects may increase the photographic speed of the films or may change the speed in one region of the spectrum at the expense of that in another. Since this effect was observed only recently, quantitative data on the extent of the effect on photographic speed are not yet available.

Experience with the above dye mixture will prove valuable in formulating other mixtures later in the program. For example, an effort must be made to find a good dye with an absorption maximum near 5500 \AA , which is the wavelength of greatest sensitivity of the eye. The present mixture has a decided window in that region, and may, therefore, have higher dye concentrations than would otherwise be necessary to achieve the same physiological effect. Another improvement may be a closer control of photosensitive agent concentration. In the present film, the CBr_4 concentration is probably considerably greater than necessary. For very high concentrations of CBr_4 , the photographic speed seems to be independent of CBr_4 concentration. However, as shown above for CHI_3 , at low concentrations, the quantum efficiency is directly proportional to the concentration of photosensitive agent. The optimum concentration should then be on the shoulder of the concentration-speed curve. This permits optimum speed and easier heat fixing.

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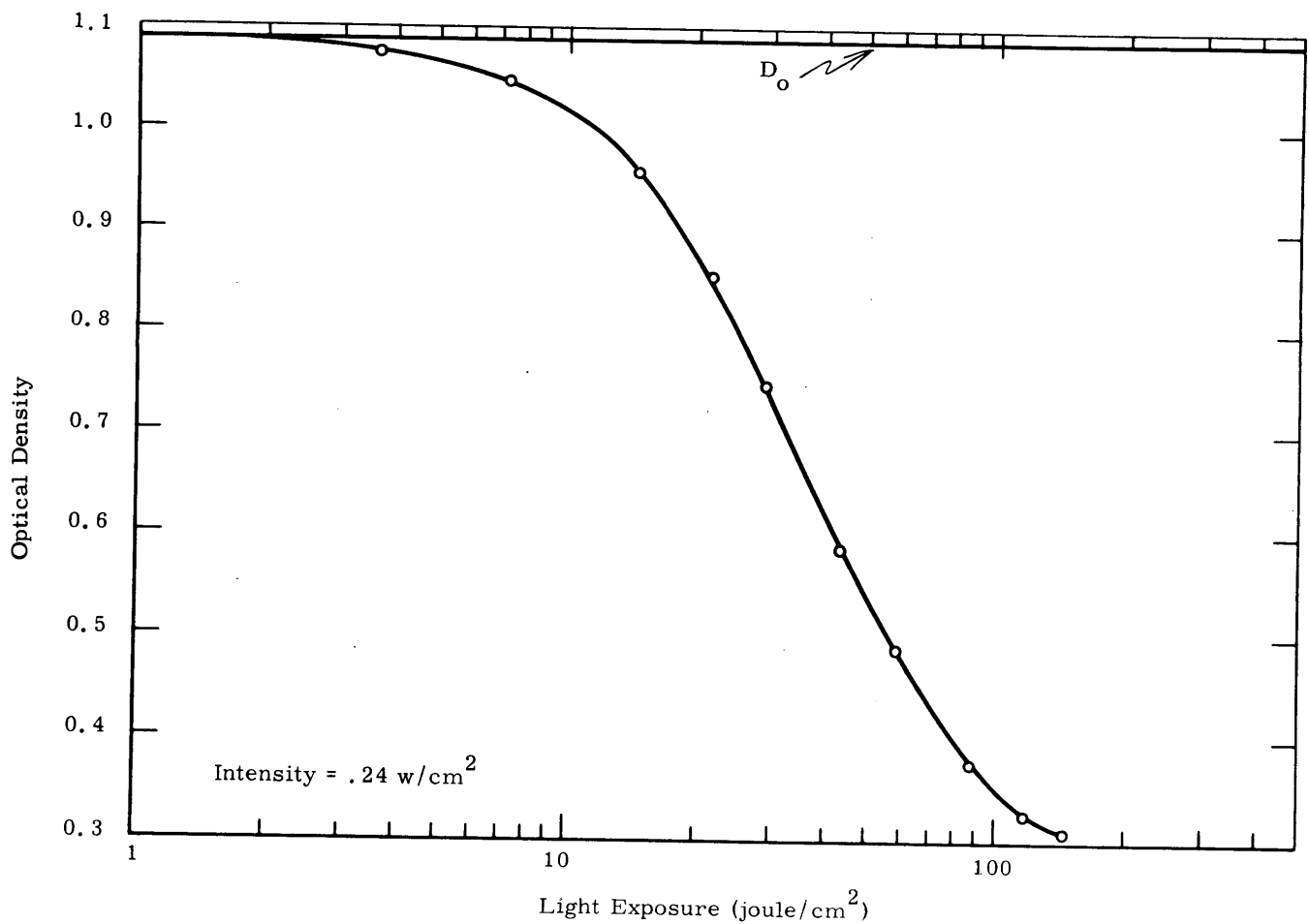
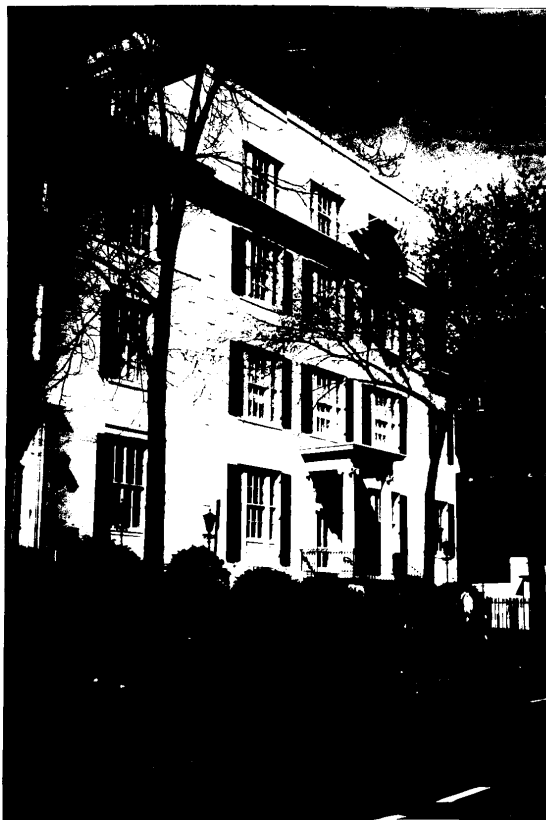
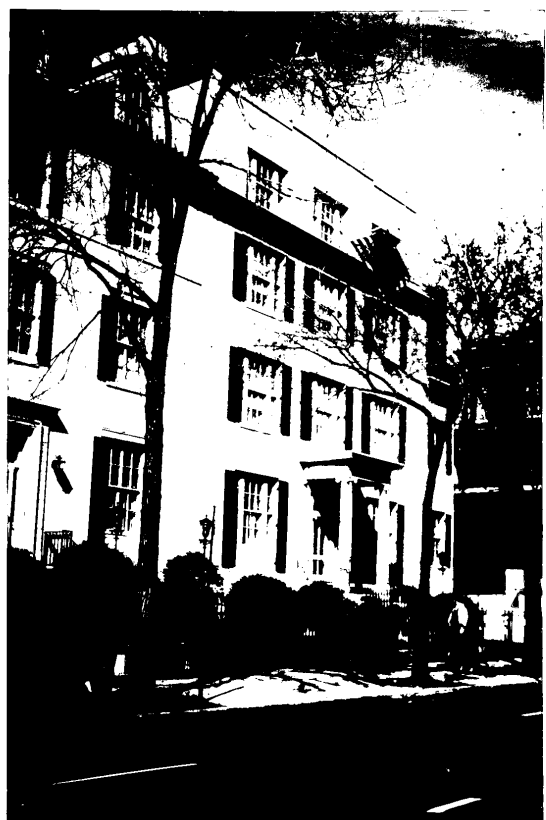


Figure 4. H & D Curve, Black and White Film



A



B

Figure 5

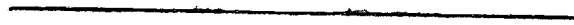


Figure 6. Sample of Black and White Film

VIII. DIRECTION OF FUTURE WORK

References to future work have been interspersed throughout this report. In this section, they will be brought together and amplified.

The most pressing task is that of definitively determining the mechanism of the reaction, and of finding whether or not a single mechanism obtained for all dyes. This is necessary for three important reasons:

A. Attaining the desired speed depends on the application of some multiplicative factor, as discussed previously. The development of such a factor, difficult under any circumstances, would be considerably more difficult if no clear picture of the mechanism were available.

B. Attaining the desired D_{\min} should be greatly facilitated by a knowledge of the end product of the bleaching reaction. Experimentally, this knowledge is obtained more easily from mechanism studies than from isolation and chemical identification of the end products.

C. The photosensitive agent should be improved, for efficiency and for ease of heat fixing. This task too will be facilitated by a knowledge of the function of this agent on the process.

Therefore, since a knowledge of the reaction mechanism will greatly expedite the solution of the most important problems, the reaction mechanism studies will take first priority in the coming months.

In addition, parametric studies will be continued, to continue building up a fund of information which will be useful in the application of the films. Quantum efficiency, action spectrum, and energy transfer studies will also be continued. These serve to throw additional light on the mechanism, and to complement the parametric work.

In parallel with the studies mentioned above, screening of new dyes will continue, and a program of polymer evaluation will be put on a more formal basis, to aid in optimizing the physical matrix for the film. In addition, techniques and equipment for the measurement of resolution will be obtained, and the effect of heat treatment on resolution determined.

The above program is designed to achieve the objectives of the proposal for Phase II of this project with optimum efficiency.

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Final Report

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